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PREDICTION OF THE FATES OF ORGANIC CHEMICALS IN BIOLOGICAL TREATMENT PROCESS - AN OVERVIEW

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16. ABSTRACT

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ABSTRACT

A program to develop methods for the prediction of organic chemical fates in activated sludge processes has been implemented. This paper presents an overview of this project. Bio-oxidation, stripping, and biomass adsorption fate mechanisms were identified as major transport/conversion mechanisms in the activated sludge process. Each mechanism was studied separately, and individual experimental protocols and kinetic models were developed. The resulting relationships were studied in lab-scale activated sludge units.

INTRODUCTION

It has been estimated that 50,000 organic chemicals are in commercial production in the United States and about 500 to 600 new organic chemicals per year are being placed into production. These chemicals and their process by-products find their way into industrial wastewaters and are often treated in biological treatment plants. Many of these organic chemicals are rapidly oxidized by biological processes, and many more can be oxidized if the treatment plant biomass is able to acclimate to the specific problem compound and establish a stable population. Still other organics are known not to undergo biological oxidation in treatment plants, but the number of these compounds has been thought to be minimal and until recently their environmental and health impacts have been unknown.

Existing industrial biological treatment plants have been designed to remove specified levels of organic pollution as measured by the conventional parameters of biochemical oxygen demand (BOD) or chemical oxygen demand (COD) to meet specified discharge criteria. Discharge criteria have often been established based on the belief that the receiving bodies possess a certain capability to assimilate BOD and that the aqueous discharge is within the assimilation capability of the natural waters. Even difficult-to-degrade organics, in this way of thinking, would eventually be converted or destroyed since the natural water ecosystem is also a biological reactor, albeit more slowly responding than biological treatment plants.

With improving analytical methodology, environmental scientists have established that many compounds persist in the environment for long periods of time. Increased emphasis has emerged related to determining the levels of specific compounds entering the environment from various sources, including biological treatment plants.

Since biological treatment facilities are engineered systems where the system design parameters (hydraulic residence time, mean cell residence time, aeration intensity, etc.) are known, it would appear that calculations or at least estimation of the fates of specific chemicals in such units should be easy to do. After all, there has been a major emphasis on chemical fate prediction in the

environment in the past decade. New data and prediction methods related to environmental fate prediction abound in the literature.

However, several problems exist that impinge on the ability to make quantitative prediction of fates of organics in activated sludge plants.

As any environmental engineer may testify, the system at play in an activated sludge plant is complex. Nearly all possible states of matter and phases may exist simultaneously in the waste feed stream and in the process. Compound or substrate concentration in each phase, as well as determination of the quantities of each phase, is necessary before predictive techniques for determining transport and conversion are employed. Furthermore, an abundance of transport/conversion rate mechanisms are known and may be important in different cases. However, the experimental data to determine the importance of these rates and, in some cases, the mathematical expressions describing these rates are not available. Data and expressions drawn from environmental fate studies may or may not apply to engineered systems.

Finally, efforts in this area have been confused by a phenomenon we term "spurious success." Some investigators have been able to apply existing theory and data to some substrates and systems to yield adequate predictions. These techniques are often ineffective when other, seemingly similar substrates exhibit much different fates in an activated sludge system. These techniques often assume equilibrium partition relationships between gas/water and biomass/water phases and apply to compounds that either strip, adsorb, or bio-oxidize readily to the mutual exclusion of the other mechanisms. Substrates that strip and bio-oxidize, for instance, do not lead to adequate predictions with these methods, even if the compounds are structurally similar to substrates well-predicted by these techniques.

It was timely for the implementation of a project aimed at integrating existing experimental and mathematical knowledge of fate prediction as applied to activated sludge processes and development of new experimental and mathematical techniques as necessary. These experimental and mathematical techniques would be applied first to individual transport/conversion mechanisms, then to continuous lab-scale activated sludge systems. The feasibility of applying experi-

mental data to yield fate predictions, directly, using mathematically based predictors, and, ultimately, fate predictions based on physical, chemical, and structural properties of the substrate were determined. This paper presents an overview of the project[1] as a whole and other papers presented at this session present more of the specifics of each mechanism study.[2,3,4]

Conceptual Approach

The process that was studied was a continuous flow completely mixed activated sludge process using coarse bubble diffusers as shown in Fig. 1. Comparison between other aeration approaches (fine-bubble diffusers and surface aerators) was left for further study. Completely mixed reactors (backmix reactors) were chosen because data collected based on these designs may be extrapolated to plug flow and batch designs by using traditional chemical reaction engineering techniques.

The process description shown in Fig. 1 is not a sufficient level of detail to allow application of mechanistic rate equations for the resolution of fate prediction. Each process stream may contain multiple phases between which the substrate may transfer. Since it is assumed that stripping, adsorption, and bio-oxidation rate mechanisms depend on the soluble concentration in the aqueous concentration, substrate residing in non-aqueous phases may be a storehouse, releasing substrate over time to the aqueous phase. A description of the physical phases or compartments present in all of the liquid process streams is presented in Fig. 2.

The compartments shown are the aqueous compartment, the gas/vapor compartment, the liquid organic compartment, and the solid compartment. The solid compartment is broken into many subcompartments relating to differing types of solids present. Pure substrate can also be present as organic liquids or solids. Transport/conversion mechanisms between compartments are shown as rate vectors, and each may be represented by a suitable rate equation.

The compartment-based system in Fig. 2 is typical of the complexity of real activated sludge processes operating on any but the most simple industrial wastewaters. However, after limiting the scope of this project to meet budget constraints, it was decided to target the objectives of this project to a more

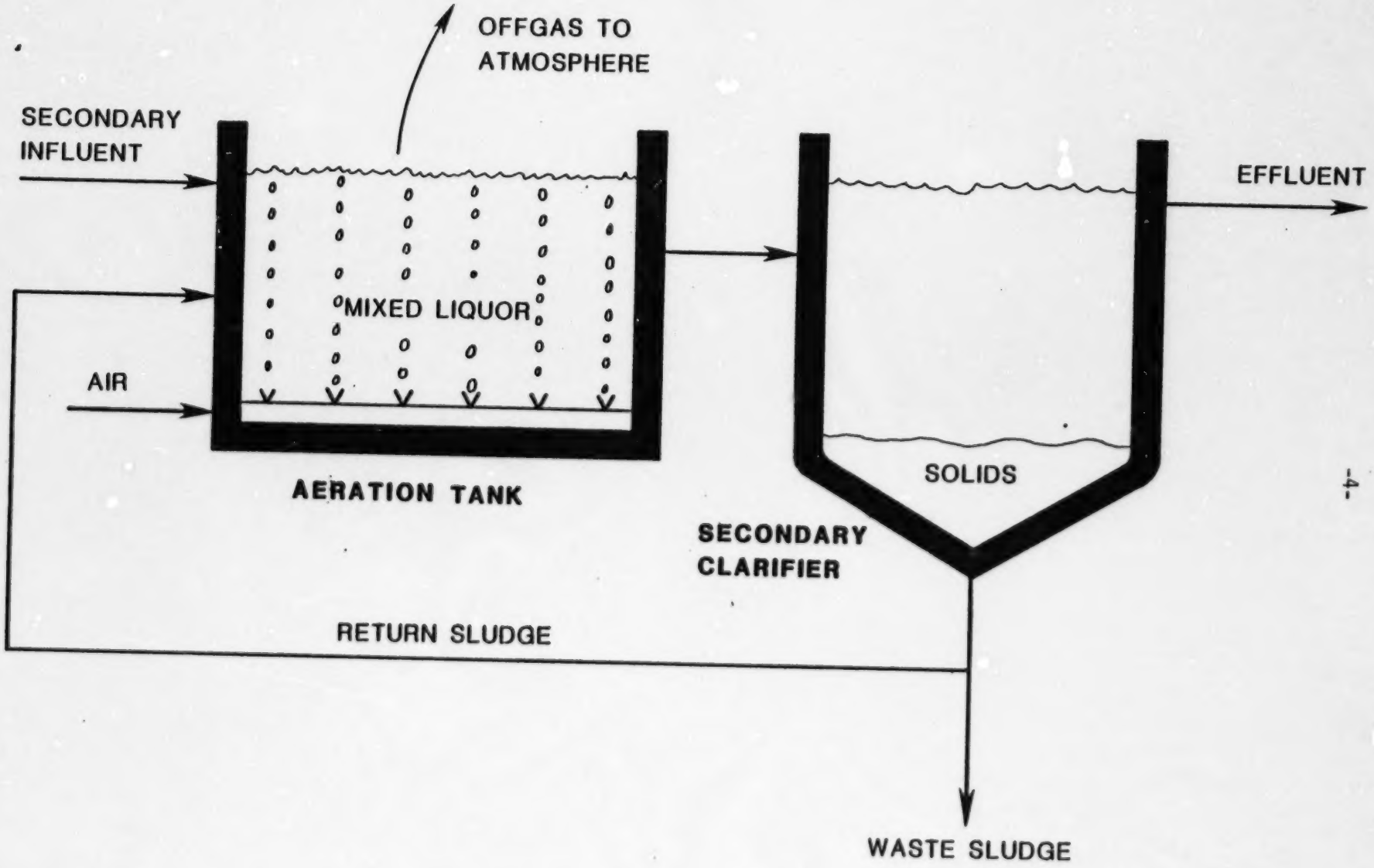

FIGURE 1. **MODEL ACTIVATED SLUDGE PROCESS**

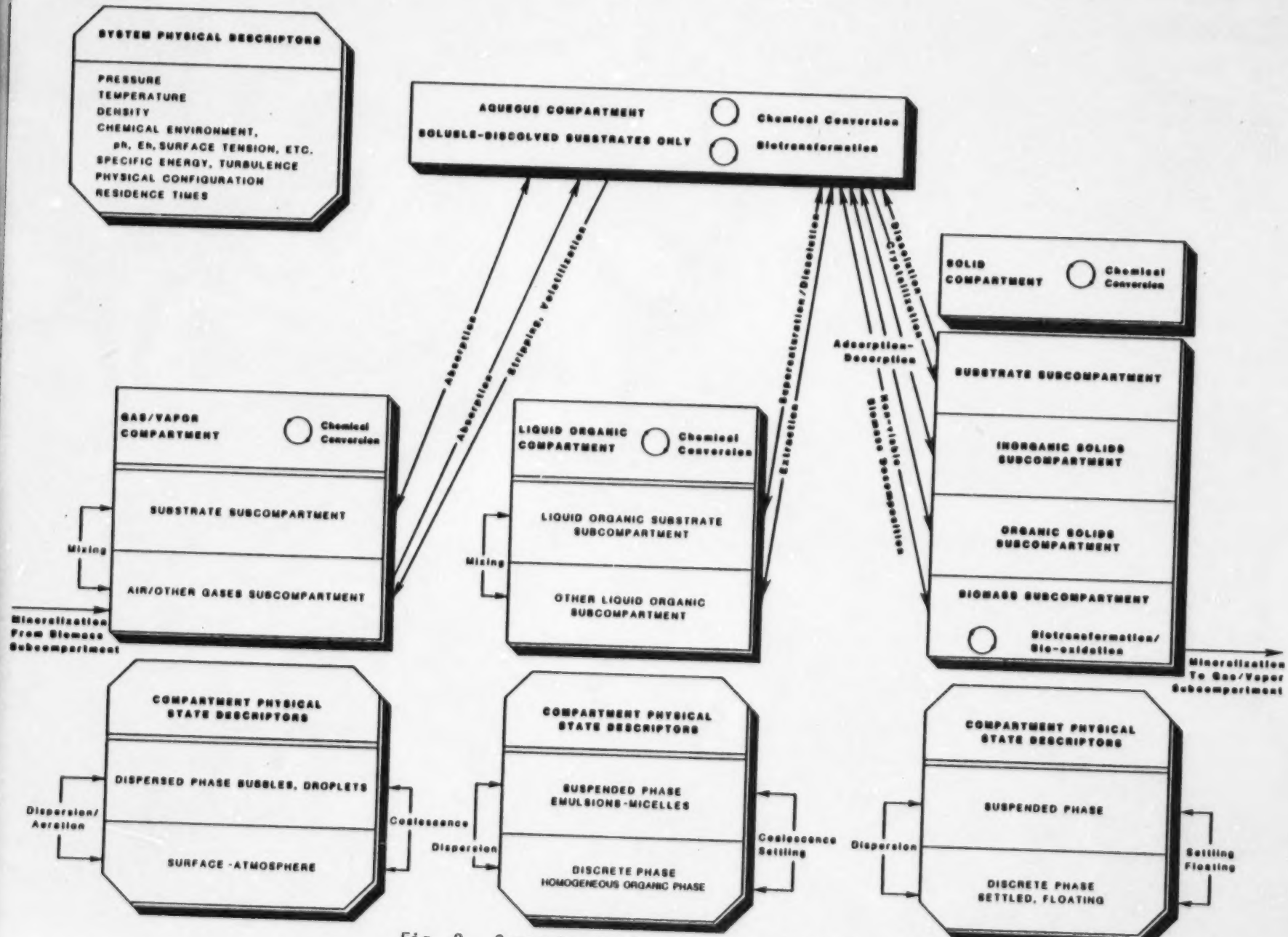

Fig. 2. Compartments in an Activated Sludge System

simplified and idealized system as shown in Fig. 3. Many compartments and sub-compartments are eliminated through the control of the wastewater influent matrix. Attention to feed makeup prevented the addition of undissolved substrate, and selection of test substrates reduced the possiblity of chemical conversion mechanisms.

The mathematical formula describing the simplified system described in Fig. 3 is as follows:

$$r^{tot} = \frac{dC_a}{dt} = r^a + r^s + r^b \qquad (1)$$

where:

r^{tot} = is the overall rate equation describing substrate concentration increases related to all mechanisms,

dC_a/dt = instantaneous rate of increase of the substrate concentration in the aqueous compartment,

r^a = the net rate equation describing substrate concentration increases related to adsorption-desorption processes in the aqueous compartment,

r^s = the net rate equation describing substrate concentration increases related to stripping, volatilization, or absorption processes in the aqueous compartment, and

r^b = the net rate equation describing substrate concentration increases related to biotransformation--bio-oxidation processes in the aqueous compartment.

dC_a = change in concentration of the substrate in the aqueous phase

dt = change in time

The net rate equation for adsorption is the difference between the adsorption and desorption rates or:

$$r^a = r^d - r^{ad} \qquad (2)$$

where:

r^d = desorption rate equation, and

r^{ad} = adsorption rate equation

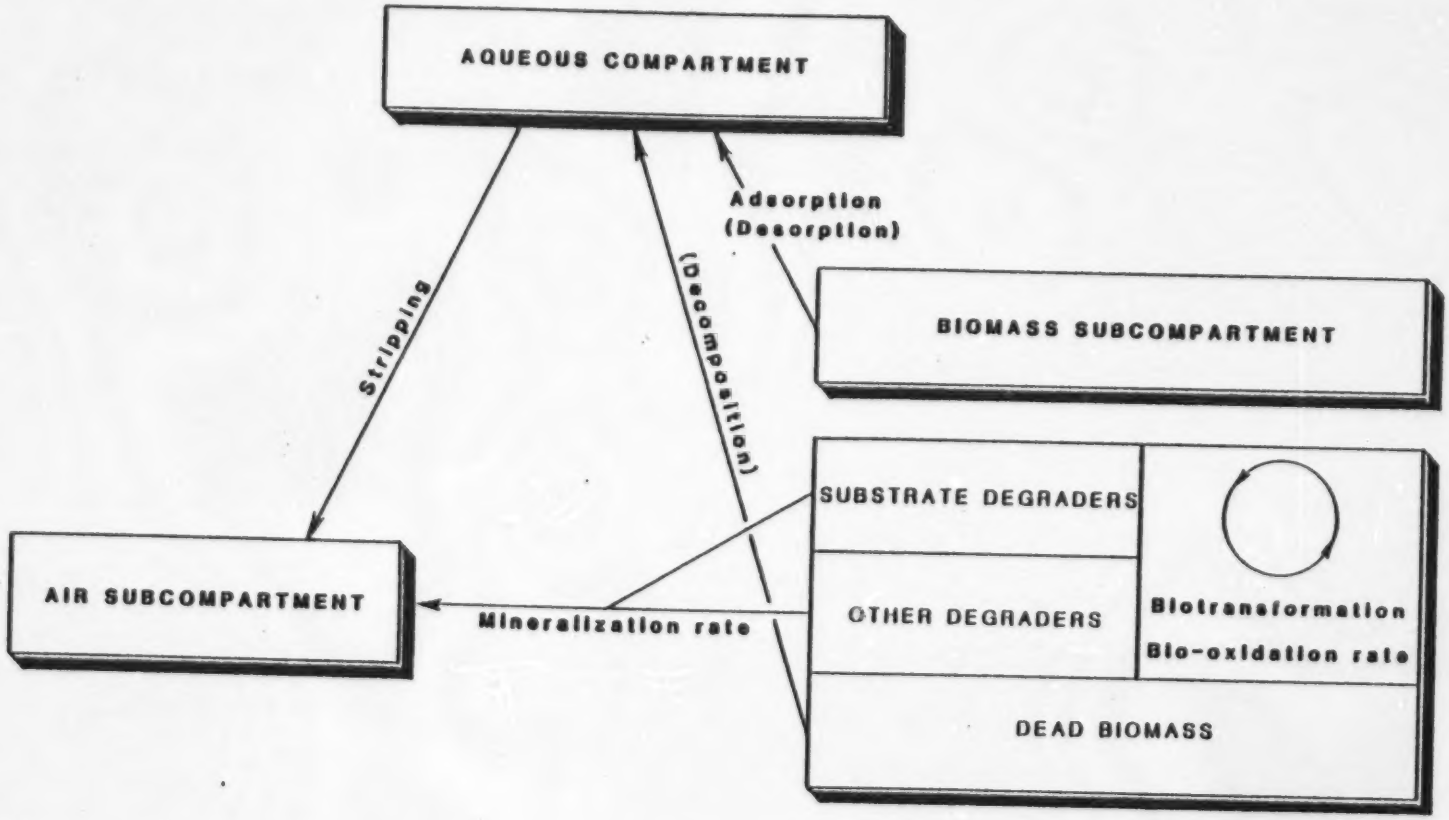

Fig. 3. Simplified System Studied in This Project

The net rate of substrate concentration increase related to stripping, volatilization, and absorption processes, r^s, has the form of:

$$r^s = r^{ab} - r^{st} - r^v \qquad (3)$$

where:

r^{ab} = the rate equation for absorption of substrate from the gas-vapor compartment into the aqueous compartment,

r^{st} = the rate equation for stripping of substrate from the aqueous compartment into the gas-vapor compartment, and

r^v = the rate equation for volatilization of substrate from the aqueous compartment into the gas-vapor compartment.

The distinction between stripping and volatilization is that stripping occurs between dispersed gas-liquid phases (bubbles, droplets) while volatilization occurs at the gas-liquid surface.

In the activated sludge process, r^{st} is assumed to be much more significant than r^v because the gas liquid interfacial area in dispersed phase systems is much greater than the continuous liquid surface. r^{ab} is assumed negligible since the concentration of substrate in the feed air is rarely significant. Therefore, in this study $r^s = r^{st}$.

The bio-oxidation - bio-transformation rate equation, r^b, can be written as a first order rate equation, a second order rate equation, and using equations derived from the Michaelis-Menten kinetic model, a first-to-zero order equation depending on substrate concentration and the substrate half saturation constant.

Once data are collected to determine the form, order, and constants in the rate equations, an overall design relationship may be used for calculating removal of substrate from the aqueous compartment and subsequent transfer accumulation in other compartments. Equation 4 may be used for complete-mixed designs and equation 5 for batch or plug-flow designs. It is assumed that liquid volume and density remains constant in activated sludge reactors.

Completely Mixed

$$HRT = C_{ao} \frac{dR_a}{-r^{tot}} \qquad (4)$$

Batch and Plug Flow

$$BHRT = C_{ao} \int \frac{dR_a}{-r^{tot}} \qquad (5)$$

where:

BHRT and HRT = the hydraulic residence time for the batch and continuous systems, respectively, (hr),

C_{ao} = the initial or feed concentration of substrates in the aqueous compartment,

R_a = the removal or conversion of the substrate from the aqueous compartment, and

$-r^{tot}$ = the overall applicable rate equation.

It is noted that the design equations of both batch and plug flow systems contain the integral of a conversion of dR_a. Conversion may be stated in terms of concentration changes (in a constant volume system). Therefore $R_a = (C_{ao}-C_a)/C_{ao}$. Also, $-r^{tot}$ is a function of C_a, except for zero order rates. In the cases of more than one major mechanism, the integral becomes difficult to analytically evaluate and the time/length based substrate concentration profile is often required to solve the relationship. The mathematics describing batch or plug flow systems inherently require experimental substrate-concentration profile data for multi-mechanism systems while the completely mixed design only requires information on C_a, since C_a is uniform throughout the reactor.

These equations, coupled with material balances for biomass growth and other system parameters (amount of air fed to liquid volume, etc.), can be used to predict the fates of organic chemicals in activated sludge plants.

Literature Review

Bibliographical information is presented in the project report.[1]

Before experimental studies in this area commenced, literature up to the fall of 1981 was surveyed to determine the state of knowledge on bio-oxidation, stripping, and adsorption rate mechanisms.

Work to investigate the literature focused on two areas. First, real mechanistic data on specific organic compounds was needed in order to base any quantitative rate equation. Second, the status of the theory of each of the transport/conversion mechanisms needed to be determined.

The data-related literature survey covered over 1000 specific organic compounds and over 200 separate data sources. Each source was screened for the type of experiment, the presence of kinetic data, and the reporting of a number of experimental variables. This information was considered essential if the data were to be used in prediction of the fate of chemicals in a treatment plant. Using a computer sorting technique, the data were analyzed to see how many data sources met our evaluation criteria. Table 1 presents the evaluation criteria applied to the data base and Table 2 shows the fraction of studies meeting the criteria. Very little data meeting these minimum criteria were available at that time.

The survey of mechanistic theory led to the collection of 36 sources in the stripping area, 13 in the adsorption area, and 59 in the bio-oxidation area. It was evident after this review that although some specific kinetic theory was available in the stripping area, the theory was unverified in actual biological wastewater treatment systems. No suitable kinetic theory of adsorption was found, and biological degradation kinetics required specific testing with the specific biomass and compound matrix of interest. As bio-oxidation kinetic rate constants were determined experimentally, they could be applied using kinetic theory. However, no effort had been evident to investigate whether the kinetic rate constants could be estimated without specific treatability testing.

Table 1. Bio-oxidation Data Quality Evaluation Criteria

Criteria	Test Method			
	Biochemical Oxygen Demand	Flask Tests	Warburg and Other Respirometric Tests	Activated Sludge Studies
Record from primary reference	X	X	X	X
Compound concentration specified	X	X	X	X
Sludge concentration specified			X	X
Mixed microbial population	X	X	X	X
Acclimated microbial population	X	X	X	X
Temperature specified	X	X	X	X
Kinetic data	X	X	X	X
Corrected for endogenous respiration	X		X	
Quantification of stripping and adsorption				X

Table 2. Results of Data Quality Assessment

Test Method	Number of Data Records Passing Criteria	Number of Compounds
Biochemical oxygen demand	1	1
Flask tests	3	2
Laboratory-scale activated sludge	3	2
Warburg and other respirometric tests	50	22

Selection of Compounds

It was realized at an early stage that a number of criteria were involved in the selection of compounds. Consideration of a class of organic compounds that shared biological degradation pathways was an overriding concern. A class of compounds in which the initial steps of bio-degradation were the same was desired. Aromatic compound degradation holds a ring cleavage step in common. This pathway appears to be common for all aromatics; therefore, aromatics were chosen as the class of compounds for study.

Criteria were developed on which to base specific compound selection, and a list of possible compounds was generated. The criteria were:

- High (low) tendency to strip
- High (low) tendency to adsorb
- High (low) tendency to bio-oxidize
- Ease of analysis
- Safe to handle
- Cost and availability of radiolabeled compound
- Member of EPA specified groupings

Criteria-related data collected on each of the possible compounds led to a list of compounds meeting all criteria. The tendency to adsorb and strip was estimated by calculations using Henry's law constant and octanol-water partition coefficients to predict maximum concentration of the compounds in the gas and biomass phases, respectively. Bio-oxidation was estimated through knowledge of the bio-degradation pathways as well as kinetic data collected in the literature survey.

Table 3 presents the compounds finally studied in each mechanism area and important physical/chemical properties for each compound.

Table 3. Compounds Studied in This Project

Compound	Stripping	Adsorption	Bio-oxidation	Lab Scale Activated Sludge Study	Henry's Law Constant (torr·liter/g-mole)	Octanol-water Partition Coefficient
Phenol	X	X	X	X	0.25	31
Toluene	X		X	X	2769	537
Aniline			X	X	0.76	8
1,4-Dichlorobenzene	X	X			1116	2455
Pentachlorophenol		X		X	2.1	132000
2,4-Dichlorophenol			X		13.4	1202
Methyl ethyl ketone	X				17.3	

Individual Mechanism Experimental Studies

The experimental studies for the individual mechanisms are described in detail in other reports and papers.[2,3,4] This paper will include only a brief description.

Stripping Mechanism -- An experimental apparatus was designed to yield scalable data and to closely simulate an operating treatment plant. A six-foot high, six-inch diameter glass column was equipped with a coarse-bubble diffuser fabricated from a stainless steel pipe cap with eight 1/32-in. diameter orifices. Air at constant humidity was fed into the system at flow rates of 0.077 to 0.308 liters per minute per liter of wastewater. These aeration rates were chosen to bracket those found in full-scale plants. Aqueous and off-gas samples were taken and analyzed to determine a material balance. Oxygen reaeration rates were also measured for each experiment. Temperature was constant at approximately 20°C; surface tension of the aqueous phase was measured for all runs.

Results from these experiments allow the following conclusions:

- Although the stripping rate and oxygen transfer rate vary in the same direction, they are not directly proportional. Various contaminants can affect the oxygen transfer rate differently from the stripping rate.
- In pure water systems, the stripping rate constant can be predicted by the compound's Henry's law constant and the gas flow to liquid volume ratio.
- The presence of surfactants, salts, oils, nonviable biomass, and other compounds can vary the stripping rate. With a few exceptions, contaminants cause a reduction in the stripping rate. Variations of ±50% of the stripping rate may be seen as a result of contaminants.

Adsorption Mechanism -- In order to measure adsorption rates on biomass, biological activity must be stopped and the stripping rate must be controlled. Otherwise, measurement of changing aqueous phase compound concentrations could also include effects of bio-oxidation and stripping. Bio-oxidation rates were eliminated from adsorption experiments by developing a technique for killing the biomass without changing its physical appearance and behavior. Lyophilization

followed by a dry heat treatment was used. Biological solids treated by the lyophilization/heat treatment protocol had flocculation and settling properties indistinguishable from live biomass. Experiments were also conducted with a "live" biomass and a relatively non-biodegradable compound, 1,4-dichlorobenzene, to compare adsorption kinetics for "live" and "dead" biomass.

The stripping mechanism was eliminated from adsorption measurements by the design and construction of a zero head space, variable-volume reactor. The volume in this reactor was varied from 5 to 9 liters by using a piston bottom. Samples were withdrawn from the reactor, centrifuged, and the liquid phase analyzed to determine an aqueous concentration/time profile. The biomass phase was also analyzed at equilibrium to check the material balance.

Conclusions relating to adsorption studies are:

- The batch experimental technique with nonviable biomass appears to give realistic results compared to tests with viable biomass.
- Adsorption kinetics for phenol and 1,4-dichlorobenzene are exceedingly fast -- too fast to measure practically (equilibrium in <4 min). Adsorption kinetics for pentachlorophenol are measurable and appear to have a two-step pattern, the first relatively fast and the second much slower.
- A simple predictive equation for low concentrations of substrate appears to be capable of predicting equilibrium concentrations of substrates based on K_{ow} and cellular lipid concentration.
- Evidence is seen for a saturation effect on equilibrium adsorption for high concentrations of substrate.

Bio-oxidation Mechanism -- It was recognized early in the program that the bio-oxidation mechanism would be the most difficult on which to develop experimental and mathematical kinetic protocols. With live biomass, it is impossible to control adsorption since adsorption (uptake) is the first step in most forms of bio-oxidation. Since bio-oxidation requires oxygen, stripping cannot be eliminated except for very short duration experiments. Early literature evaluations proved the inherent variability in biomass and the ease of arriving at widely differing kinetic rates in differing studies, depending on the biomass history and acclimation, substrate concentration, and wastewater matrix.

After much planning, it was decided to develop a batch kinetic assay using radiolabeled compounds and a standard acclimated biomass. Compound mineralization, compound disappearance, and intermediate buildup were measured. A population assay was developed to measure the fraction of viable biomass and the population of specific compound degraders (e.g., phenol degraders).

This approach enabled the collection of bio-oxidation rate constants as well as data to support inferences on enzyme concentrations, to determine extent of acclimation, and to provide basic data on which to compare relative kinetics of related aromatic compounds. Results are presented in another paper.[4]

Lab-Scale Activated Sludge

Design and Operation -- Studies were conducted with laboratory-scale activated sludge (LAS) units to attempt to verify the predictive fate methods which had previously been developed for stripping, adsorption, and bio-oxidation.

Two complete-mix continuous flow activated sludge units were constructed of 6-in. ID pyrex pipe with stainless steel end flanges. Each reactor was operated at a liquid volume of 11 liters. External clarifiers were fabricated of 3.5 in. ID pyrex pipe and had an operating volume of 1.5 liters. Coarse bubble diffusers were constructed of 3.5 in. stainless steel pipe caps with four 1/32-in. orifices drilled at a 1-in. radius from the center. A diagram of the experimental system is shown in Fig. 4. Composite feed and effluent samples were collected by continuously pumping from the feed drum and clarifier overflow line. Air samples were collected once a day for 3-hr in caustic bubblers (phenol, aniline, and pentachlorophenol) or for 40 min in Tedlar bags (toluene). Toluene samples collected in Tedlar bags were subsequently pumped through the caustic bubblers for determination of CO_2 in the vent gas. Grab samples of mixed liquor were collected once a day immediately before the initiation of air sampling.

Wastewater feed to the system consisted of a kraft pulp mill foul condensate wastewater spiked with both "cold" and ^{14}C-labeled test compound, inorganic nutrients, and a phosphate buffer solution. This study was based on mechanism behavior in an actual industrial wastewater stream and foul condensate represented a wastewater with somewhat constant composition over time.

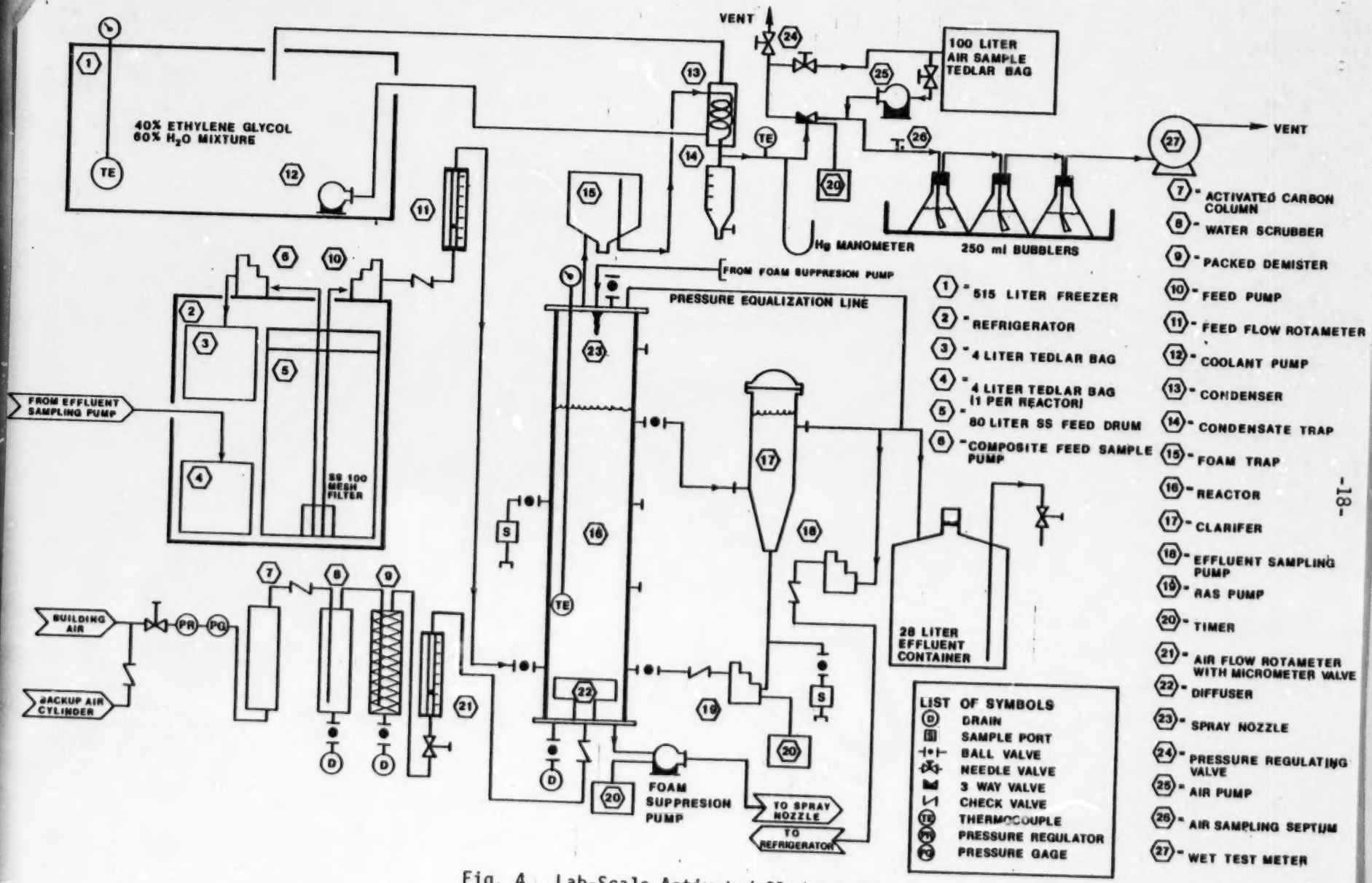

Fig. 4. Lab-Scale Activated Sludge Units

A summary of the system operating parameters is shown in Table 4, and a summary of substrate removal data is shown in Table 5. Examination of the data in Table 5 indicates very high overall removal efficiencies for phenol, toluene, and aniline while pentachlorophenol was found to be very resistant to removal from the process wastewater.

Overall Compound Fates -- Insight regarding the fates of the individual test compounds may be gained from a simultaneous interpretation of data in Tables 6 and 7. The removal of the test compounds by bio-oxidation was calculated by subtracting the amount recovered in the effluent, vent gas, and waste from the feed. Data in Table 7 do not differentiate among the possible fates of ^{14}C; the ^{14}C may be present as the original compound, a metabolite, $^{14}CO_2$, or as cell mass. However, data in Table 6 show that for phenol, toluene, and aniline, very small percentages of the parent compound were recovered in either the waste sludge or the effluent; indicating that the ^{14}C was not recovered in the form of the parent compound in these sampling locations. Therefore, it appears that a large percentage of the ^{14}C recovered from biological solids was transformed and converted into cellular mass. For these three test compounds, soluble ^{14}C in the sludge and effluent is therefore presumed to be predominantly in the form of a metabolites of the parent compound. Greater than 99% of the ^{14}C collected in the bubblers was precipitated as $Ba^{14}CO_3$ for selected samples, indicating that virtually all of the ^{14}C collected in the bubblers was from $^{14}CO_2$ rather than a volatile metabolite. Both the test compound and ^{14}C material balances for pentachlorophenol show that approximately 6 to 8% of the feed compound was adsorbed to the waste solids and greater than 73% of the feed was found in the effluent.

Phenol -- Phenol was never detected in either the effluent or the bubblers at an analytical detection limit of 0.50 mg/L. The performance of the reactors operated at mean cell residence times (MCRT) of 4.8 and 8.8 days was almost identical in terms of both phenol removal and the fate of ^{14}C. Average phenol loadings on biological solids were 108.5 µg/g MLSS and 47.8 µg/g MLSS for reactors 1 and 3, respectively.

Aniline -- Examination of the material balances for the parent compound and ^{14}C reveal that the fate mechanisms for aniline are almost identical to the fate mechanisms for phenol. Aniline is readily bio-degraded with over 55% of the

Table 4. Summary of Lab-Scale Activated Sludge Units Average Operating Parameters

Start Date	End Date	Test Compound	Reactor No.	Mean Cell Residence Time (days)	Feed Flow (ht/day)	Hydraulic Residence Time (hr)	MLSS (mg/L)	MLUSS (mg/L)	pH	Mixed Liquor Temperature °C	Mixed Liquor DO (mg/L)	Air Flow (lit/min)
06/01/83	06/08/83	Phenol	1	4.8	9.41	28.0	2,221	1,960	7.00	22.2	5/2	2.50
			3	8.8	10.15	26.0	3,827	3,347	6.95	22.6	4.9	2.43
06/22/83	07/22/83	Toluene	1	4.6	10.45	22.8	1,281	1,169	6.96	20.6	3.5	2.03
			3	9.1	11.18	23.6	2,369	2,109	6.98	21.1	2.1	2.04
07/29/83	08/12/83	Aniline	1	5.0	11.32	23.3	1,685	1,525	6.82	21.1	5.4	2.08
			3	10.0	11.11	23.8	2,551	2,322	6.79	21.1	4.5	2.04
08/22/83	09/02/83	Pentachlorophenol	1	4.9	10.38	25.4	1,367	1,275	6.80	22.0	6.5	2.01
			3	9.3	10.98	24.0	2,290	2,066	6.81	21.7	5.6	2.02

[a]Does not include data for period 07/02/83 through 07/11/83. Units were operated in a maintenance mode and limited analytical data was collected during period.

Table 5. Summary of Lab-Scale Activated Sludge Units Average Substrate Removal Performance

Start Date	End Date	Test Compound	Reactor No.	Test compound				TOC			BOD_5		
				Influent (mg/L)	Mixed Liquor (mg/L)	Effluent (mg/L)	Removal Efficiency (%)	Influent (mg/L)	Effluent (mg/L)	Removal Efficiency (%)	Influent (mg/L)	Effluent (mg/L)	Removal Efficiency (%)
06-01-83	06-08-83	Phenol	1	985.9	<0.50	<0.50	>99.95	1334	240	82.0	2394	75	96.9
			3	985.9	<0.50	<0.50	>99.95	1334	183	86.3	2394	44	98.2
06-22-83[a]	07-22-83	Toluene	1	194.6	<0.30	<0.06	>99.97	525	133	74.7	717	28	96.1
			3	194.6	<0.26	<0.29	>99.85	525	142	73.0	717	31	95.7
07-29-83	08-12-83	Aniline	1	109.0	<0.10	<0.10	>99.91	460	135	70.7	665	7	98.9
			3	109.0	<0.10	<0.10	>99.91	460	127	72.4	665	8	98.8
08-22-83	09-2-83	Pentachlorophenol	1	8.6	7.4	7.6	11.6	536	196	63.4	895	123	86.3
			3	8.6	7.3	8.0	7.0	536	165	69.2	895	34	96.2

[a] Does not include data for period 07-02-83 through 07-11-83. Units were operated in a maintenance mode and limited analytical data was collected during this period.

Table 6. Test Compound Material Balance Summary for LAS Study

Test Date	End Date	Test Compound	Reactor No.	Percent of Feed					
				Bio-oxidation	Sorbed to[b] Waste Solids	Soluble In Waste Activated Sludge	Soluble Effluent	Vent Gas	Percent of Feed Compound Recovered
06-01-83	06-08-83	Phenol	1	>99.92	0.007	<0.002	<0.052	<0.017	<0.078
			3	>99.93	0.002	<0.002	<0.050	<0.016	<0.070
06-22-83	07-02-83[a]	Toluene	1			<0.001	<0.04	<11.6	
			3			<0.001	<0.16	<11.9	
07-29-83	08-12-83	Aniline	1	>99.88	0.01	<0.003	<0.07	<0.04	<0.12
			3	>99.88	0.01	<0.001	<0.07	<0.04	<0.12
08-22-83	09-02-83	Penta-chloro-phenol	1	0.00	7.45	4.23	89.70	<0.23	101.61
			3	0.00	6.61	2.51	94.60	<0.22	103.94

[a]Does not include data for period 07-02-83 through 07-11-83. Units were operated in a maintenance mode and limited analytical data was collected during this period.

[b]Includes effluent TSS and waste activated sludge.

Table 7. ^{14}C Material Balance Summary for LAS Study

Start Date	End Date	Test Compound	Reactor Number	Percent of Feed					
				Waste[a] Solids	Soluble In Waste Activated Sludge	Soluble Effluent	Vent Gas	Remaining in Reactor and Clarifier at End of Run	Percent of Feed ^{14}C Recovered
06-01-83	06-08-83	Phenol	1	17.72	0.38	14.04	55.29	10.92	98.35
			3	12.55	0.50	13.15	55.83	15.93	97.96
06-22-83	07-22-83	Toluene	1	25.02	0.17	5.07	67.51	2.76	100.53
			3	16.49	0.73	5.97	70.41	4.13	97.73
07-29-83	08-12-83	Aniline	1	17.66	0.56	14.01	55.56	10.48	98.27
			3	15.94	0.31	12.34	57.30	13.88	99.77
08-22-83	09-02-83	Pentachloro-phenol	1	7.78	2.40	73.00	0.50	9.36	93.04
			3	6.07	1.47	78.15	0.81	10.84	97.34

[a]Includes effluent TSS and waste activated sludge.

feed ^{14}C converted to $^{14}CO_2$. Aniline was never detected in either the effluent or the bubblers at an analytical detection limit of 0.10 mg/L. Instrument changes during the last 3 days of the aniline run resulted in analytical detection limits of 0.01 mg/L. During this period, the average concentration of aniline in the effluent was found to be 0.032 and 0.028 mg/L for reactors 1 and 3, respectively. Average loadings of aniline on biological solids were 30.6 and 33.2 µg/g MLSS for reactors 1 and 3, respectively.

Toluene -- Toluene was chosen as a model compound to study the relative rates of stripping and biodegradation. Sorption to solids was not measured for toluene since toluene has a relatively low octanol-water partition coefficient and it was estimated that overall removal due to sorption was negligible. Since sorption to solids was not measured, no estimate of the percent of the feed toluene bio-oxidized could be made based on the conventional analysis. However, analysis of the ^{14}C data indicates that toluene is more readily biodegraded than either phenol or aniline as indicated by the high percentage of feed ^{14}C recovered as $^{14}CO_2$ in the bubblers. Analysis of bubbler trains for reactors 1 and 3 revealed that less than 0.60 and 0.33% respectively of the ^{14}C collected could be attributed to toluene.

Vent gas samples for toluene analysis were collected in 100 liter Tedlar bags for 40 min each day. Samples were analyzed for vapor phase toluene concentration, and the gas bag contents were then pumped through caustic bubblers for CO_2 collection. Vent gas concentrations of toluene were found to be highly variable for both reactors, with concentrations ranging from <0.75 ppm_v to 160 ppm_v. Material balances indicated that 11.6 and 11.9% of the toluene fed to reactors 1 and 3, respectively, was stripped in the off gas. However, the toluene concentration in the vent gas was below the detection limit of 0.75 ppm_v for approximately 30% of the samples from each reactor. At a vent gas concentration of 0.75 ppm_v, less than 0.4% of the toluene in the feed was stripped from the mixed liquor.

Pentachlorophenol -- Pentachlorophenol was found to be completely resistant to bio-oxidation as indicated by the high percentage of feed pentachlorophenol recovered in the reactor effluents. Minimal acclimation time was allowed prior to pentachlorophenol startup so that the adsorption mechanism might be better

tested in the LAS runs. Adsorption onto biological solids was the major pathway for the removal of pentachlorophenol from both LAS systems. Both the test material balance and the ^{14}C balance indicate that approximately 6 to 8% of the pentachlorophenol fed to the system is lost via adsorption to waste solids.

Validation of Stripping Predictive Fate Method (PFM)

The PFM which was developed for the stripping rate constant is as follows:

$$K_a{}^{st}a = \frac{Q_a}{V} \cdot 3.71 \times 10^{-3} H_c{}^{1.045} \qquad (6)$$

where:

$K_a{}^{st}a$ = stripping rate constant (hr^{-1}),

Q_a = air flow (L/min),

H_c = Henry's law constant (torr • L/g-mole), and

V = reactor volume (L).

Assuming first order kinetics, the vent gas concentration can be predicted from the following equation:

$$C_v = \frac{K_a{}^{st}a \cdot C_a \cdot V \cdot \frac{1g}{1000\ mg} \cdot \frac{1g\text{-mole}}{MW\ g} \cdot \frac{22.4\ L}{g\text{-mole}} \cdot \frac{10^6\ ppm_v}{L\ toluene/L\ air}}{Q_a \cdot \frac{60\ min}{hr}} \qquad (7)$$

Simplifying,

$$C_v = \frac{K_a{}^{st}a \cdot C_a \cdot V \cdot 373.3}{Q_a \cdot MW}, \qquad (8)$$

where:

C_v = concentration in the vent gas (ppm_v),

C_a = soluble concentration in the mixed liquor (mg/L), and

MW = molecular weight of compound (g/g-mole).

Equation 8 was used to predict the vent gas concentrations from the LAS reactors for the toluene study. The analytical detection limit for the experimental

system was 0.05 mg/L for the aqueous phase. At these detection limits, a maximum vent gas concentration of 2.97 ppm_v would be calculated using equation 8. The results of this analysis are shown in Table 8. Nine data points were available for which the soluble toluene concentration in the mixed liquor was above the detectable limit. Five of the predicted vent gas concentrations were within ±50% of the measured value. Of the twelve data points for which C_a was below the detectable limit, nine of the measured vent gas concentrations were below the maximum value predicted by equation 8.

Stripping losses during LAS studies for phenol, aniline, and pentachlorophenol were negligible, as shown in Table 6. Stripping losses for these studies were estimated in order to verify the stripping PFM for low volatility compounds. These calculations were performed using average values of air flow rate and soluble mixed liquor concentrations measured during the studies with each compound. The stripping PFM was also used to project the percentage of the feed compound which could be stripped if no other removal mechanism was active, i.e., no adsorption or bio-oxidation. This analysis for a continuously fed complete-mixed reactor takes the form:

$$C_a = \frac{C_{ao}}{1 + K_a{}^{st}{}_a\,(HRT)}$$

where:

C_a = aqueous phase effluent concentration (mg/L),

C_{ao} = feed concentration (mg/L),

HRT = hydraulic Residence Time (hr), and

$K_a{}^{st}{}_a$ = stripping rate constant (hr^{-1}).

Results of these analyses are presented in Table 9. Estimated and measured removals by stripping are in agreement for both phenol and aniline; however, measured quantities of pentachlorophenol were significantly less than predicted by the model. A possible explanation for the anomaly is that pentachlorophenol is predominately in the form of pentachlorophenate at a pH of 7.0. No Henry's law constant was available for pentachlorophenate. However, it is likely to be

Table 8. Validation of Stripping PFM for Toluene Based on Daily Average Data

Date	Reactor	Air flow (L/min)	Off gas (ppm_v)	Mixed liquor (mg/L)	Predicted off gas (ppm_v)
06/24/83	1	2.02	<0.75	<0.05	<2.97
06/28/83	1	2.18	166.	4.30	256.
06/29/83	1	2.22	17.0	<0.05	<2.97
06/30/83	1	2.15	99.0	1.40	83.2
07/12/83	1	1.88	2.60	0.06	3.56
07/13/83	1	1.70	1.40	<0.05	<2.97
07/14/83	1	1.75	<0.75	<0.05	<2.97
07/15/83	1	1.60	<0.75	<0.05	<2.97
07/18/83	1	1.85	11.0	0.20	11.9
07/21/83	1	2.30	<0.75	<0.05	<2.97
06/24/83	3	2.20	3.20	<0.05	<2.97
06/28/83	3	1.98	190.	4.70	279.
06/29/83	3	2.05	14.0	<0.05	<2.97
06/30/83	3	1.96	46.0	0.80	47.6
07/11/83	3	2.00	83.0	1.30	77.3
07/12/83	3	2.08	<0.75	<0.05	<2.97
07/13/83	3	2.00	<0.75	<0.05	<2.97
07/14/83	3	1.92	<0.75	<0.05	<2.97
07/15/83	3	1.97	<0.75	1.10	65.4
07/18/83	3	1.88	21.0	0.30	17.8
07/21/83	3	2.30	0.75	<0.05	<2.97

Table 9. Estimation of Stripping Losses for LAS Systems

Compound	Reactor	Predicted K_s (hr^{-1})	Percent of Feed		
			Actual Measured	Estimated Based on Measured Mixed Liquor Concentrations	Estimated for No Bio-oxidation or Adsorption Losses
Phenol	1	1.98×10^{-4}	<0.017	<0.0003	0.55
	3	1.93×10^{-4}	<0.016	<0.0003	0.50
Aniline	1	5.26×10^{-4}	<0.04	<0.001	0.44
	3	5.16×10^{-4}	<0.04	<0.001	0.44
Pentachlorophenol	1	1.47×10^{-3}	<0.23	3.21	3.60
	3	1.48×10^{-3}	<0.22	3.02	3.43

lower than the H_c for pentachlorophenol, thus explaining the low recovery of the compound in the vent gas.

Validation of Adsorption PFM

The adsorption PFM which has been developed incorporates both the rate of adsorption and the equilibrium partitioning between solid and liquid phases. First stage adsorption rate coefficients were shown to be relatively high in the batch studies, with first order initial adsorption rate coefficients over 75.6, 6.95, and 41.28 hr^{-1} determined for phenol, pentachlorophenol, and 1,4-dichlorobenzene respectively. Adsorption rate constants may be significantly higher than these values, with the maximum rate constant measurable being more a function of the minimum time required to process the sample (4 to 10 min) than a physical property of the chemical. Attainment of equilibrium at low concentrations has been reported by other investigators to take less than 30 min.[5,6]

A relationship that has been used to describe the equilibrium partitioning between sludge solids and an aqueous phase is:

$$C_s = K_a C_a \qquad (9)$$

where:

C_s = equilibrium loading on the sludge solids (µg/g),

C_a = equilibrium aqueous phase concentration (µg/L), and

K_a = adsorption distribution coefficient (L/g solids).

This equation is similar to the empirical Freundlich adsorption isotherm equation:

$$C_s = K_f C^{1/n} \qquad (10)$$

where:

K_f, n = empirical coefficients

for values of n near unity, equation (10) is identical to equation (9) and K_f is equivalent to K_a.

Another commonly used adsorption isotherm equation, the Langmuir equation is based on the assumption that the solid phase has a finite capacity, i.e., a maximum loading which will not be exceeded. The Langmuir isotherm has the form:

$$C_s = \frac{a\ b\ C_a}{1 + b\ C_a} \qquad (11)$$

where:

a, b = empirical constants.

It can be shown that as C_a becomes large, a is equivalent to the maximum loading. As C approaches zero, the numerator of equation (6) approaches 1 and equation (11) is equivalent to equation (9) with

$$a \cdot b = K_a \qquad (12)$$

An isotherm equation has been proposed of the form:

$$C_S = \frac{K_{ow} \cdot f \cdot C_a}{\rho_L} \qquad (13)$$

where:

K_{ow} = octanol water partition coefficient (dimensionless),

f = lipid weight fraction of biological solids (µg lipid/µg dry solids), and

ρ_L = density of lipids (g/L).

Equation 13 is equivalent to equation 9, where

$$K_a = \frac{K_{ow}\ f}{\rho_L} \qquad (14)$$

A summary of the adsorption data collected during the LAS study is shown in Table 10. The average loading for each of the compounds follows the trend of increasing with increasing K_{ow} value. However, aniline shows a higher distribution coefficient than pentachlorophenol, although the K_{ow} value for pentachlorophenol is 5 orders of magnitude greater than for aniline. Average values of

Table 10. Summary of Sludge Loading Data for LAS Study

Compound	Date	Reactor No. 1			Reactor No. 3		
		Sludge Loading (µg/g)	Soluble Concentration in Mixed Liquor (µg/L)	Distribution Coefficient (L/g)	Sludge Loading (µg/g)	Soluble Concentration in Mixed Liquor (µg/L)	Distribution Coefficient (L/g)
Phenol	06/01/83	<94.1	<500				
	06/02/83	<41.7	<500		<32.7	<500	
	06/08/83	<189.7	<500		<62.9	<500	
Aniline	08/08/83	<51.2	<100		<36.7	<100	
	08/08/83	<27.9	<100		<33.4	<100	
	08/10/83	22.5	32	0.70	28.5	19	1.50
	08/11/83	22.6	23	0.98	30.7	30	1.02
	08/12/83	28.9	51	0.57	36.8	104	0.35
Pentachlorophenol	08/22/83	1441	7700	0.19	1080	7000	0.15
	08/23/83	1529	9500	0.16	1240	9800	0.13
	08/24/83	2429	8800	0.28	2585	8600	0.30
	08/25/83	2318	8800	0.26	2464	7800	0.32
	08/26/83	2364	5800	0.41	2418	5500	0.44
	08/28/83	1225	6800	0.18	1534	5800	0.26
	08/29/83	1264	7700	0.16	1132	7000	0.16
	08/30/83	1208	7100	0.17	943	7100	0.13
	08/31/83	2270	6800	0.33	2349	6100	0.39
	09/01/83	3179	6500	0.49	2439	7700	0.32
	09/02/83	2409	6100	0.40	1628	6100	0.27

sludge loadings and aqueous phase concentrations were used to project distribution coefficients using equation (13). The results of this analysis are shown in Table 11.

Pentachlorophenol sludge loading data for both the batch tests and the LAS study indicate that the aqueous phase concentration may be in the range where the sludge has achieved a saturation condition. A Langmuir isotherm constructed using data from both the batch and the continuous studies supports this observation. The Langmuir equation may be transformed to yield:

$$\frac{C_a}{C_s/C_a} = \frac{1}{ab} + \frac{1}{a} C_a \qquad (15)$$

A plot of the batch pentachlorophenol loading data and the average loading for each of the two continuous reactors is shown in Fig. 5. A similar analysis was conducted for batch data for 1,4-dichlorobenzene and for aniline data from the LAS systems. The results of these analyses are presented in Table 12. Each of these sets of data appear to fit the Langmuir model, as evidenced by the high correlation coefficients (r) obtained.

The distribution coefficients (K_a) for low concentrations in the aqueous phase may be determined from the Langmuir equation as shown by equation (12). The log (K_a) obtained by this method was plotted versus log (K_{ow}) for PCP, DCB, and aniline. Data from other investigators and K_a values calculated using equation (14) were plotted on the same graph and are shown in Fig. 6. Data for phenol was included by utilizing the average distribution coefficient obtained during the batch test since experimental data yielded too narrow a range of equilibrium aqueous phase concentrations of the test compared to estimate the Langmuir isotherm parameters.

Data reported by Pellazari are in the form of Freundlich K_f values. Average values of n for this data set were generally close to unity and may be neglected with the assumption that the log (Freundlich K) values on Fig. 6 may vary by ±50%.

Data in Fig. 6 indicate that predictive equation (14) is in close agreement with distribution coefficients calculated from the Langmuir isotherm equation for PCP

Table 11. Evaluation of Adsorption Equilibrium Equation

Compound	Average Loading (µg/g)	Average Aqueous Concentration (µg/L)	Observed K_a (L/g)	Predicted K_a (L/g)
Phenol	<70.2	<500	>0.14	<0.007
Aniline[a]	28.3	43	0.65	0.0018
Pentachlorophenol	1884	7277	0.26	29.29

[a]Analysis uses only data points for which C_a > detectable limit.

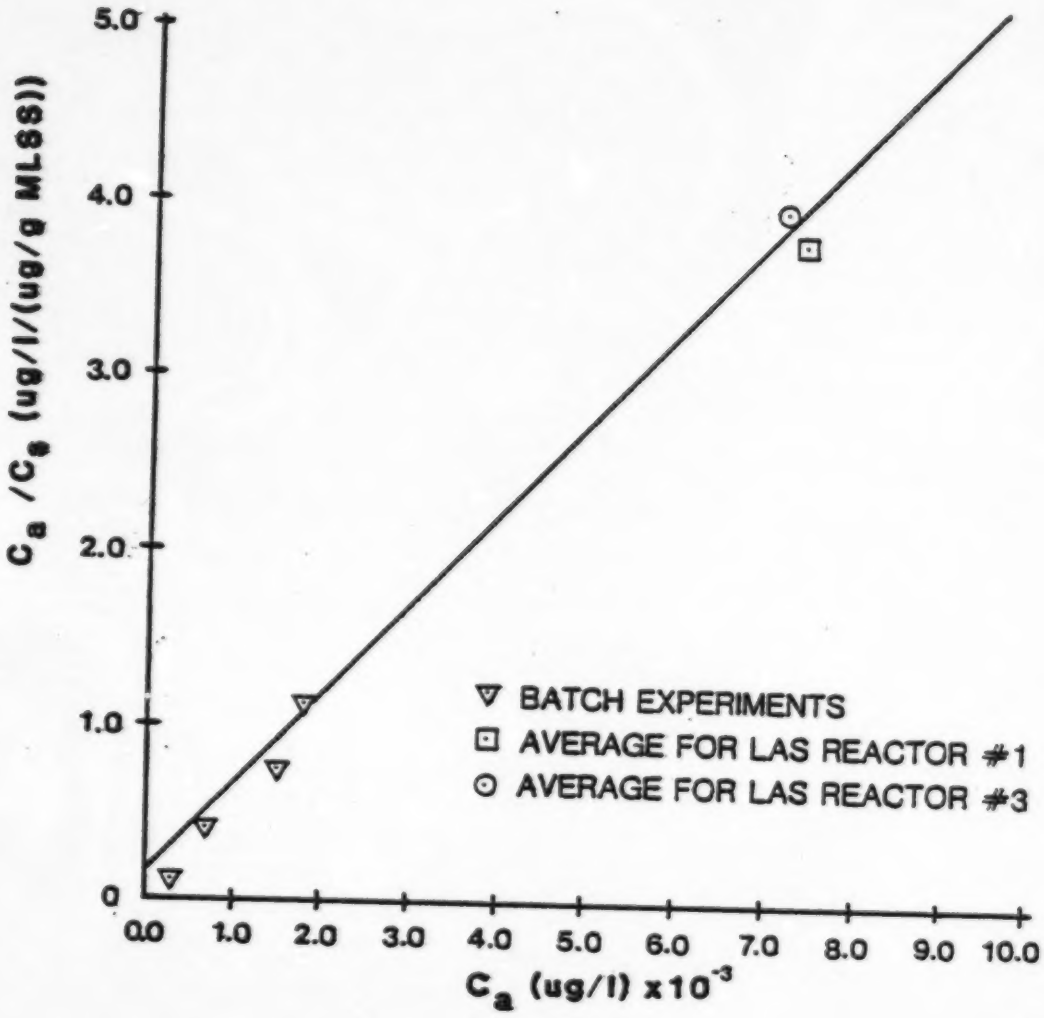

Fig. 5. Langmuir Isotherm Parameter Estimation for Pentachlorophenol

Table 12. Langmuir Isotherm Parameters

Compound	a	b	Correlation Coefficient for Equation (8) (r)
Pentachlorophenol	1908	8.52×10^{-3}	0.99
1,4-Dichlorobenzene	11560	8.48×10^{-5}	0.97
Aniline	42	5.73×10^{-2}	0.97

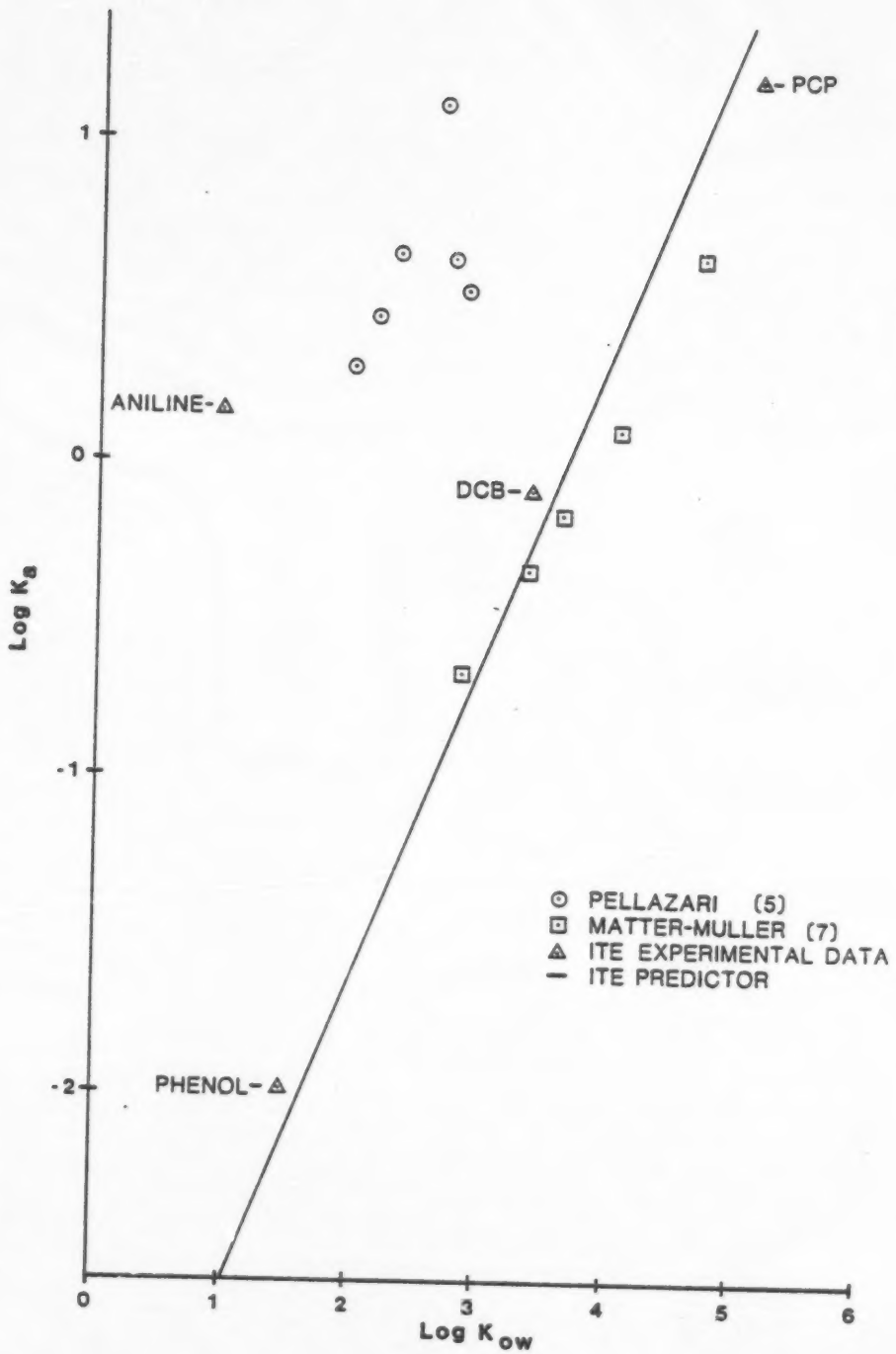

Figure 6. Log (K_a) versus Log (K_{ow}).

and DCB and with data reported by Matter-Muller.[7] This conclusion should be experimentally verified by performing adsorption isotherm studies for compounds with a wide range of K_{ow} values. Aqueous phase concentrations should be varied over several orders of magnitude to verify the assumption that a linear relationship exists between K_{ow} and distribution coefficients at low concentrations and that a saturation effect does occur at relatively high aqueous phase concentrations.

Validation of Biological Oxidation Predictive Fate Methods

Mixed liquor samples from the LAS systems were analyzed by a static assay procedure at the University of Tennessee to determine mineralization rates. Procedures for conducting the mineralization assay are described in detail in another paper.[4] Initial concentrations used in the batch tests were 40, 130, and 100 mg/L for phenol, toluene, and aniline, respectively. Incubation times of 4, 24, and 8 hr were used for phenol, toluene, and aniline respectively.

Mineralization rates were calculated by the following equation:

$$R_{BM} = \frac{f_m \cdot C_{ao}}{BHRT} \qquad (16)$$

where:

R_{BM} = biological mineralization rate (mg/L-hr of test compound),
f_m = fraction of feed ^{14}C converted to $^{14}CO_2$ in time t,
C_{ao} = concentration of test compound at start of incubation time, and
BHRT = incubation time (hr).

If mineralization is assumed to be a first order reaction, the mineralization rate constant may be calculated as follows:

$$K_m = \frac{\ln \ (1/1-f_m)}{BHRT} \qquad (17)$$

Average mineralization rates and mineralization rate constants were also calculated for the LAS reactors using the material balance data presented in Tables 4 and 7. The mineralization rate in the continuous reactors was calculated as follows:

$$R_{BM} = \frac{f_m \cdot C_{ao}}{HRT} \qquad (18)$$

where:

f_m = fraction of feed ^{14}C converted to $^{14}CO_2$, and

HRT = hydraulic residence time (hr).

The first order mineralization rate constant for the complete mix continuous flow LAS reactors was calculated as follows:

$$K_m = \frac{[1.0/(1.0-f_m)] - 1}{HRT} \qquad (19)$$

The results of this analysis are presented in Table 13. Batch mineralization rates and rate constants are the averages for 5, 5, and 10 observations for each reactor for phenol, toluene, and aniline respectively. Mineralization rates for phenol and toluene were found to be significantly lower in the batch reactors than in the continuous systems.

Mineralization rates for phenol and toluene were found to be significantly lower in the batch reactors than in the continuous systems. Mineralization rates observed in the continuous reactors are not directly comparable from compound to compound since the average concentration of the test compound in the feed, with average concentrations of 986, 195, and 109 measured for phenol, toluene, and aniline, respectively. For example, both phenol and aniline LAS systems were shown to have approximately 56% conversion of feed ^{14}C to $^{14}CO_2$; however, the mineralization rates vary approximately in proportion to the ratios of the feed concentrations of the respective test compounds. However, the mineralization rate constants are comparable on a quantitative basis and are relatively close for phenol and aniline for the continuous systems. The values of mineralization rate constants determined in the continuous systems would rank the 3 compounds in the order toluene>aniline>phenol in terms of the percent conversion of the parent compound to CO_2.

Mineralization rates obtained in the batch reactors were significantly lower for phenol and toluene than those obtained in the continuous systems while the mineralization rates for aniline were 57% and 33% higher in the batch tests than

Table 13. Comparison of Mineralization Rates and Mineralization Rate Constants in Batch and Continuous Feed Biological Reactors

Compound	Reactor	MLSS (mg/L)	Batch		Continuous (LAS)	
			Rate (mg/L•hr)	Rate Constant (hr^{-1})	Rate (mg/L•hr)	Rate Constant (hr^{-1})
Phenol	1	2221	0.75	1.95×10^{-2}	19.	4.41×10^{-2}
	3	3827	0.40	1.02×10^{-2}	21.2	4.86×10^{-2}
Toluene	1	1281	0.63	5.15×10^{-3}	5.16	8.22×10^{-2}
	3	2369	0.55	4.46×10^{-3}	5.80	10.1×10^{-2}
Aniline	1	1685	4.10	4.97×10^{-2}	2.60	5.36×10^{-2}
	3	2551	3.50	4.10×10^{-2}	2.63	5.65×10^{-2}

in the continuous tests for reactors 1 and 3, respectively. The depression of the mineralization rates observed in the batch reactors appear to contradict the conventional Monod model, in which biological oxidation rates increase with increasing concentration up to a maximum limiting rate. Preliminary work with phenol indicated increasing rates of phenol mineralization at concentrations up to 120 mg/L.[4]

Several factors may contribute to the differences in mineralization rates observed in the batch and continuous reactors. Initial concentrations of the test substrate were much higher in the batch tests than the concentrations in the mixed liquor in the continuous tests. If mineralization rates are truly first order, high mineralization rates would be expected at the concentrations employed in the batch reactors. If mineralization rates are zero order and independent of concentration, rates measured in the batch reactor would have been expected to more closely approximate those measured in the continuous systems. These observations lead to the conclusion that the initial phenol and toluene concentration used in the batch reactors may have been inhibitory to the biomass from the continuous reactors. Concentration differences in the batch and continuous systems may have also caused a shift in relative percentages of ^{14}C utilized in cellular growth and $^{14}CO_2$ production.

Rate studies on phenol disappearance yielded results similar to those observed for phenol mineralization.[4] Batch tests conducted at initial phenol concentration of 30 mg/L yielded a phenol disappearance rate of 1.75 mg/L-hr over an 8-hr period while average phenol disappearance rates of approximately 36.5 mg/L-hr were observed in the two continuous reactors.

The differences noted in the batch and continuous systems illustrate that batch assays must be conducted over a range of concentrations in order to provide predictive methods for continuous systems. Also, experiments designed to determine the overall reaction order for the mineralization process should be incorporated into the assays.

Problems and improvements in degrader population assay techniques are discussed in another paper.[4]

Feasibility of Fate Predictor for Organics in Activated Sludge Systems

The basic goal of this project was to integrate existing knowledge and data relating to organic fate prediction and test the feasibility of application to activated sludge processes. The effort considered 3 separate approaches to fate prediction. The first approach relates to predictions based on actual fate data and related experimental methods. Fates may be determined for each system of importance if adequate experimental methodology exists.

The second approach uses data on specific compounds and deterministic understanding of the fate mechanisms to predict fates for different compounds and systems.

The last approach uses deterministic understanding coupled with data on physical, chemical, or structural properties of the specific chemicals to predict fates of different chemicals from property data alone.

Our estimation of the feasibility of each of these approaches for the individual mechanisms is summarized in Table 14. Stripping measurement by sampling and analysis is presently feasible. It should be noted that gas analysis is more reliable for determining stripping rates of low Henry's law compounds while liquid analysis is more reliable for high Henry's law compounds. Stripping prediction with deterministic predictors is feasible if the stripping predictor presented in this work[2] is validated on more compounds. Further studies on contamination effects are also needed for more compounds and system configurations. This prediction is also based on physical properties of the substrate. Therefore, predictions based on substrate properties are also feasible with further work.

We are optimistic that adsorption experimental data determination is feasible with the methods employed in this project.[3] This needs to be confirmed for more compounds over a wider range of concentration. Modifications to include experimental determination of the saturation effect are required. Similarly, we are optimistic that these data may be applied using deterministic predictors. Work targeted at predictions of the saturation concentration is required. Again, the prediction is based on physical properties and measured levels of lipids. If a satisfactory property-based prediction of saturation concentration becomes evi-

Table 14. Summary of the Feasibility of Organic Fate Predictions for Activated Sludge Processes

Application	Determination of Experimental Data	Deterministic Predictors Based on Experimental Data	Deterministic Predictors Based on Substrate Properties
Stripping	Feasible at present	Feasible with further work	Feasible with further work
Adsorption	Optimistic with further work	Optimistic with further work	Optimistic with further work
Bio-oxidation	Possible with further work	Possible with further work	Inconclusive-further work
All three mechanisms-			
Continuous activated Sludge systems			
Lab scale	Feasible at present[a]	Possible with further work	Inconclusive-further work needed
Full scale	Optimistic with further work[b]	Possible with further work	Inconclusive-further work needed

[a]Assuming a known, controlled biomass that minimizes compartments.

[b]Assuming that complete compartment sampling and analysis is not needed. Some compartments and rates are not significant.

dent, then physical-, chemical-, or structural-based predictions may be feasible.

Present experimental approaches, with modification, appear to be capable of determination of bio-oxidation mineralization rate data. Modifications include time-course experiments designed to yield data for determination of the order of the rate and improved methods for determining viable degrader populations in mixed cultures.[4] These experiments must be conducted over a broad range of concentrations to examine concentration dependence of the rates observed.

Substrate bio-transformation (compound disappearance) rates measured in batch systems appear to be substantially lower than rates measured in continuous systems. This needs further investigation since specific compound disappearance rates are required for quantitative fate prediction.[4] The deterministic understanding of bio-oxidation rates is sufficient so that when the experimental determination of disappearance rates and the quantitative determination of degrader populations becomes feasible, the deterministic prediction should also be possible. The prediction of bio-oxidation rates from substrate property data may be possible, but no suitable data on substantially different types of compounds were collected. As more experimental data are collected on different compounds, the ability to assess substrate property-based bio-oxidation prediction will be enhanced.

Collection of combined experimental data on continuous systems is feasible in controlled lab experiments, but may be difficult in full scale systems if many compartments and subcompartments are present and if other transport/conversion rates are important. Studies related to sampling and analysis of substrates in subcompartments and the importance of hitherto unstudied rate mechanisms are needed. Experimentally based predictions should be possible as the problems noted above with the individual mechanisms are cleared up. Complete fate prediction based on compound properties for continuous systems depends on resolution of problems in adsorption and bio-oxidation property-based predictors.

If the property prediction of bio-oxidation rates proves elusive, then methods on stripping and adsorption may still be used to correct experimental data allowing determination of corrected bio-oxidation rates. This may still lead to

methodology allowing estimation of fates in full scale treatment plants within a certain error factor.

The authors are optimistic that with continued efforts in this area, the "art" of biological treatment plant design may become more of a science. Basic limitations of the process for specific compound removal, an understanding of multimedia environmental effects, and specific plant design improvements may be elucidated.

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